ARSENIC AND HEAVY METALS IN SOILS AND GROUNWATER FROM Au MINE TAILINGS IN RODALQUILAR (ALMERÍA, SE SPAIN)

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1. Introduction

In SE Spain, the mining of base metals and Au-Ag, mainly during the nineteenth century, generated huge quantities of mine wastes such as tailings, mine-waste calcines, heap leach impoundments and smelting slags. These wastes were abandoned at hundreds of mine sites and, because of the oxidation process of pyrite and other sulfide minerals, they represent a potential threat to the environment (Wray, 1998; Viladevall et al., 1999; Navarro et al., 2000, 2004 and 2006; Robles-Arenas et al., 2006; Navarro et al., 2008a and 2008b).

The problems associated with unremediated mine sites containing sulfide minerals included the liberation of metals (Al, Cd, Cu, Fe, Hg, Mn, Ni, Pb and Zn) and metalloids (As, Sb, Se and V) and occasionally the generation of acid mine drainage (AMD).

Thus, soluble metal sulfate salts may play a key role in the generation of acid mine drainage in epithermal deposits such as Summitville (Plumlee et al., 1999), in which jarosite, halotrichite and other sulfates were identified. The mine waters draining these high-sulfidation (HS) deposits and/or mine waste dumps can contain very high concentrations of Al, As, REE, Co, Ni, Cr, U, Th and Be, due to low pH. However, adit waters collected in dry periods or water draining propylitically altered rocks may contain lower metal concentrations and near neutral pH values (Plumlee et al., 1999).

In exploited epithermal high-sulfidation deposits such as Rodalquilar, mineralization is characterized by the geochemical association Au-Ag-Cu-As-Bi-Te-Sn (Seal and Hammarstron,2003). These are elements that can be mobilized in the soil, sediments, groundwater, and surface waters. The effluents and leachates from these mine sites can have pH levels between 2.0 and 8.9, Fe concentrations between 0.01 and 50000 mg/L, an Al concentration between 0.001 and 5000 mg/L, and sulfate concentrations from 0.8 to 100000 mg/L. Furthermore, significant concentration of Cu, Zn, Co, Ni, Cd and As are not uncommon (Seal and Hammarstron, 2003).

In similar situations, the migration of contaminants such as As, Cu, Zn, Pb and Cd is controlled by the presence of secondary phases. In the case of As these secondary phases may be amorphous Fe-sulfoarsenates, jarosite-beudantite (Gieré, et al., 2003), schwertmannite (Fukushi et al., 2003) or Fe oxyhydroxides (Sracek et al., 2004; Courtin-Nomade et al., 2005). Moreover, during dry periods the weathering of As-bearing sulfides may produce secondary Fe oxyhydroxides (goethite, ferrihydrite) and sulfates (jarosite), which are efficient scavengers of As oxyanions (Savage et al., 2000).

The objectives of this study are the following:

- To determine the geochemical features of the environmental impact of the abandoned tailings in the Rodalquilar mining area.
- To determine the extension of the main contaminants around the waste deposits, in sediments and in groundwater.

- To define the geochemical processes controlling the mobilization of contaminants, especially As, from the main waste impoundment to the groundwater.

2. Site description

The old mining district of Rodalquilar is located in the Sierra del Cabo de Gata (Fig. 1) at an altitude of 0-300 m above sea level in a semi-arid region 40 km east of the city of Almería. The main Rodalquilar deposit is the first documented example of caldera-related epithermal Au mineralization in Europe (Hernández et al., 1989; Sänger-von Oepen and Fiedrich, 1991; Arribas et al., 1995). Mining in this region started in the nineteenth century with the exploitation of the Pb-Zn-Ag (Au) epithermal veins of San José, 10 km south of the study area. The exploitation of low-sulfidation epithermal veins at Rodalquilar (Las Niñas) began towards the end of the nineteenth century.

The main period of exploitation took place between 1943 and 1966 by the Spanish government's company ADARO, which operated in the Cerro Cinto area by open pit and in some of the low-sulfidation epithermal veins (Consulta, Mª Josefa, Triunfo, Las Niñas, Ronda and Resto, etc.) by underground mining. During this period the main tailings dump was created as a result of the ore cyanidation treatment at the Denver plant. This led to an uncontrolled impoundment of waste over an area of approximately 50 ha. The most recent mining operation was carried out by St. Joe-Transacción between 1989 and 1991, using a heap leaching facility near the Cerro Cinto open pit. At present (2008), there is no mining activity; the area is now part of the Cabo de Gata national park.

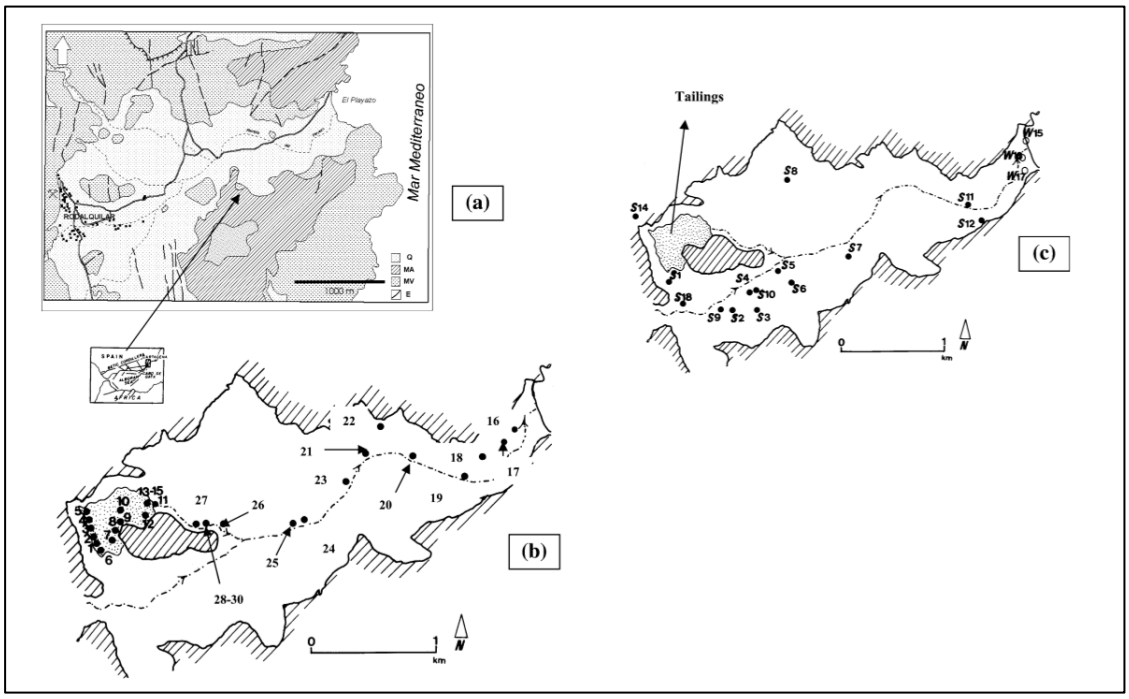

Figure 1 a. Syntethetic geological map of Rodalquilar area *E* faults, *MV* tertiary volcanics, *MA* Miocene limestones, marls and conglomerates, *Q* recent fluvial terraces. Modified from Arribas (1993). **b**. Location sediment, soil and tailing samples. **c**. Groundwater and superficial water samples. W16 and W17 surface water of lagoons, W15 sea water

2.1 Regional geology and ore deposits

The high- and low-sulfidation deposits of Rodalquilar are associated with Miocene calc-alkalic volcanic rocks of the Almería-Cartagena volcanic belt. The volcanic rocks in the Rodalquilar district comprise pyroxene and hornblende andesites, ash-

flow tuffs, postmineralization pyroxene andesite flows, and flow breccias (Fig. 1). In the eastern margin of the Rodalquilar caldera there is an alluvial-colluvial quaternary system that ends at the Mediterranean Sea.

The ore deposits consist of low-sulfidation Pb-Zn-Ag (Au) quartz veins along the north-south-trending faults and high-sulfidation Au-(Cu-Te-Sn) ores that are enclosed in areas of acid sulfate alteration (Sänger-von Oepen et al., 1990; Arribas et al., 1995). These high-sulfidation ores are found in the shallowest parts of the central core of hydrothermal activity (about 10.4 Ma) and are associated with silicified rocks, found at depths of 100-300 m. They occur in advanced argillic zones (quartz-alunite-jarosite) surrounding the cores of vuggy silica and enclosing most of the Au deposits (Arribas et al., 1995). The majority of primary Au mineralization (high sulfidation) is composed of chalcedonic quartz veins (elemental Au and pyrite rich Au) and hydrothermal breccias with high Te and Sn concentration, as well as secondary Au associated with Fe oxides, scorodite and jarosite.

2.2 Mine wastes

Ore cyanidation treatment during the periods 1930-1936 and 1943-1966 led to a period of uncontrolled tailing dumping close to the town of Rodalquilar. This became the main mine waste impoundment and during these periods the amount of waste there was evaluated at 1500000 t (Hernández, 2002). The tailings were deposited above the unconfined aquifer of Playazo creek and consisted of several terraces with a thickness of up to 10 m. They are typically red and composed of fine particles derived from grinding to a size of <63 μm (Wray, 1998). The mechanical dispersion of fine particles by rain-water runoff and wind has transported the contaminant particles to Playazo creek and the houses in the town of Rodalquilar.

A geochemical study by Wray (1998) revealed that the dominant mineralogy of tailings is quartz, kaolinite, alunite and jarosite. The study also demonstrated that Mo, Sb, Te, Bi and As are found at elevated concentrations in stream sediments. High concentration of Cu, Pb and Zn have also been reported. An analysis by Moreno et al. (2007) of fine particles (<10 μm) by X-ray diffraction and SEM showed that the fine fraction is dominated by silica, Al-Si clay, alunite, jarosite and oxidized iron minerals associated with high concentration of As. Preliminary results of the environmental impact of the Rodalquilar tailings were reported by Navarro et al. (2007).

2.3 Climate and hydrology

The climate in the Cabo de Gata region is characterized by average rainfall of 175-250 mm/year, the lowest in the Iberian Peninsula, most of which occurs between October and March. The average annual temperature is between 15 and 22 ºC. The main body of water in this area is Playazo creek, which because of the semi-arid climate is a non-permanent fluvial stream. Rainfall events are often sporadic and may mobilize the contaminants of the tailings in two ways: by surface runoff at the waste dump slopes and by infiltration and subsequent leaching of the waste dumps.

The alluvial aquifer of Playazo creek shows a thickness of 8-20 m, and the grain size of the deposits vary between fine sand, gravel and boulders. Also, there is a semi-confined aquifer, which may be associated with the presence of a geothermal system of low enthalpy. The alluvial materials include quartz, calcite, aragonite, albite, dolomite, spinel and shcherbakovite (NaK(Ba,K)Ti2(Si2Ox)2 as dominant mineral phases. The upper alluvial aquifer is enclosed at depth both laterally and partially by volcanic impermeable materials (Fig. 1). The alluvial aquifer is composed of materials derived from the surrounding bedrock and contains fragments of andesites and ignimbrites, occupying a width of 0.5-2 km and a length of 4 km, approximately.

The transmissivity of the aquifer, calculated from pumping tests and using the equation of Logan (Logan, 1964), was estimated to be between 6 and 10 m2/day. The water table is located 9-14 m below the ground and an average Darcy velocity of 0.021 m/day was calculated using an average hydraulic conductivity of 1.75 m/day and a hydraulic gradient of 0.012. Assuming the porosity of the alluvial materials to be 0.10, the mean pore water velocity can be estimated as 0.21 m/day. In the groundwater system the main recharge input is precipitation and surface water, that may recharge the aquifer from Playazo creek during wet periods. The aquifer flows into the Mediterranean Sea at Playazo beach (Fig. 1).

3. Methods

3.1 Sampling and analyses of sediments, tailings and soils

The mineralization, mine wastes and soils were manually extracted to obtain samples of approximately 1.5 kg. These samples comprised 12 samples of outcropping mineralization and mining wastes, and 32 samples of sediments, tailings and soils (Fig. 1). The mining wastes (host-rock and low grade stockpiles) had been deposited around the main mining works and the mine tailings were located near the town of Rodalquilar (Fig. 1). Mining wastes, mineralization, tailings, sediments and soil samples were passed through a jaw crusher to a particle size of 10 mesh, quartered, pulverized in an agate mortar, rehomogenized and repacked in plastic bags. Au, Ag, As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, Hg, Ir, La, Lu, Na, Ni, Nd, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Th, Tb, U, W, Y and Yb were quantitatively analyzed by instrumental neutron activation analysis (INAA), which involves bombarding the unaltered samples with neutrons. Mo, Cu, Pb, Zn, Ag, Ni, Mn, Sr, Cd, Bi, V, Ca, P, Mg, Tl, Al, K, Y and Be were analyzed by ICP-OES. These analyses used a “near total” digestion employing HF, $HClO_4$, HNO_3, and HCl to get as much of the sample into solution and the resulting metals are determined by ICP-OES at Actlabs (Ontario, Canada).

3.2 Mineralogical determinations

Mine waste, mineralization, sediments and soil samples were studied using binocular microscopy, transmitted and reflected light microscopy and X-ray diffraction (XRD) using a Bragg-Brentano PANalytical X’Pert PRO Alpha 1 geometry diffractometer (radius = 240 mm). Also, the microtextures of any thin sections were examined using a scanning electron microscope. These techniques enabled us to identify the mineral phases and later analyze the major and trace element concentration of the most abundant minerals.

3.3 Sampling and analyses of groundwater

Eighteen surface water and groundwater samples (Fig. 1) were collected from lagoons, mine shafts and agricultural wells (August 2004), the depths of which ranged from between 6 and 38 m, from a saturated zone of variable thickness.

The pH, redox potential (Eh; mV), temperature and electrical conductivity (EC; µS/cm) were corrected using standard solutions and measured in situ with portable devices (HACH model sensION TM378). The groundwater and leachate samples were filtered with a cellulose nitrate membrane with a pore size of 0.45 µm. The samples for cation analysis were later acidified to pH<2.0 by adding ultra-pure HNO_3. The samples were collected in 110 ml high-density polypropylene bottles, sealed with a double cap and stored in a refrigerator until analysis. The groundwater samples were obtained after purging each well, using a bailer sampler and the submersible pumps of agricultural wells.

The metal concentrations were measured with ICP using ICP-MS at the ACTLABS laboratories. The concentrations of chloride, nitrate and sulfate (in a second, untreated sample) were analyzed by ion chromatography. The alkalinity of the

waters was analyzed by titration. Standard reference material NIST 1640 (ICPMS) was used to confirm accuracy.

4. Results

4.1 Mineralogical results

An X-ray diffraction (XRD) analysis, binocular microscope analysis, EDAX electron microscope analysis and ore microscope image revealed the mineralogical nature of the tailings; the dominant mineralogical fractions were silica, alunite and arsenian pyrite (Table 1). These minerals were derived from the auriferous quartz extracted during the periods 1930-1936 and, more significantly, 1943-1966 from the Cerro Cinto open pit and low-sulfidation veins. Besides, the mineralogical analysis indicates the presence of albite, illite and possibly iron oxides as primary phases, and kaolinite, jarosite, okenite, schulenbergite and whitlockite as secondary phases. The quantification of arsenian pyrite metal concentration indicates a concentration of 0.8 wt% As, 52-53 wt% S, 44-46 wt% Fe, 0.1-1.9 wt% Cu and 0.1 wt% Zn.

The mining wastes obtained from the main areas that were mined (Cerro Cinto, Consulta and Las Niñas) and those close to the tailings deposit showed the presence of quartz, jarosite, galena, arsenian pyrite, chalcopyrite, sphalerite, orthoclase, gold, nantokite and alunite as main primary phases, and goethite, jarosite, hematite, pumpellyite, anglesite, ferrihydrite, covellite and scorodite as secondary phases (Table 1). Other mineral phases detected in the Rodalquilar area were barite, smectite, calaverite, tellurite, rodalquilarite, enargite, cassiterite, tetraedrite, bismutite and bornite (Arribas et al., 1995).

Moreover, sulfate-Fe-Al salts with high concentration of As (110 mg·kg-1), Cd (6.8 mg·kg-1), Zn (1070 mg·kg-1), Cu (1664 mg·kg-1), Mn (908 mg·kg-1), and low-to-medium concentration of Sb (4.1 mg·kg-1), Ni (41 mg·kg-1), Pb (82 mg·kg-1) and Bi (4 mg·kg-1) were detected at ephemeral AMD pools.

4.2 Geochemical results

The analysis of sampled tailings and sediments revealed high concentrations of Au, Ag, As, Bi, Cu, Fe, Mn, Pb, Se, Sb, V and Zn (Table 1), which were above the metal concentration of non-contaminated soils. Such soils have low concentration of these metals, in comparison with contaminated materials. The contaminant of greatest environmental concern is As, which showed a mean concentration of 679.9 mg·kg-1 in the tailings. The highest concentration of As in the tailings was 1410 mg·kg-1, and in the sediments of Playazo creek this concentration was 345.5 mg·kg-1.

The high As concentration may be explained by the presence of arsenian pyrite, associated with auriferous ore. This is the case with other gold deposits (Savage et al., 2000) and it seems to be associated with the weathering crusts of ferric oxides and Fe-oxyhydroxides (Moreno et al., 2007). Therefore, during weathering, the substitution of As into pyrite may be responsible for the rapid oxidation and dissolution of arsenian pyrite (Savage et al., 2000), which liberates As and other pollutants into the pore water and seepages, that may be released from tailings during wet periods. The presence of As in the tailings material, also, may be associated with Fe-bearing particles, probably ferric oxide and ferric oxyhydroxide, which contain around 1% As (Moreno et al., 2007).
In tailings, the concentration of copper, zinc and cadmium is high (mean concentration of 202, 472.9 and 0.8 mg·kg-1, respectively), and, also, in sediments (172.5, 241.2 and 1.1 mg·kg-1, respectively). The high concentrations of these metals may be explained by the presence of nantokite, sphalerite, chalcopyrite and covellite in the processed ore. Thus, the concentration of these metals in the mining wastes and the ore samples is high, particularly in the low-sulfidation quartz veins samples (Table 2).

In both tailings and sediments, the concentrations of antimony are high (mean concentration of 141.6 mg·kg-1and 53.5 mg· kg-1, respectively). Antimony is also found in high concentrations in Fe-fine particles of the tailings material (Moreno et al., 2007). Lead has elevated concentrations in both tailings and sediments (mean concentration of 924.1 mg·kg-1 and 379.2 mg·kg-1, respectively). The presence of anglesite, an alteration product of galena, may help to explain the elevated concentration of Pb in tailings and sediments.

In tailings, high concentrations of Au and Bi were detected (mean values of 472.3 µg kg-1 and 22.7 mg·kg-1, respectively), indicating that the efficiency of the metal extraction process was poor. The concentration of Au in the ore was moderate (4420-11900 mg·kg-1, Table 2). Hernández (2002) reported that the ore processed during the period 1956-1966 had a mean Au concentration of only 1.56-4.38 mg·kg-1.

The mean concentration of zinc was moderate both in tailings (472.9 mg·kg-1) and in sediments (241.2 mg·kg-1), derived from the presence of sphalerite. The elevated concentration of Cd seem to be associated with the presence of sphalerite, which explains the Cd concentrations of up to 661 mg·kg-1 found in the low-sulfidation ore samples enriched with sphalerite (Table 2).

Table 1:Concentrations of metals and metalloids in tailings sediments in Rodalquilar (Almería, Spain)

	Au	Ag	As	Ba	Bi	Cd	Cu	Hg	Fe	Mn	Pb	Se	Sb	V	Zn
Tailings															
R1	511	0.9	1,410	100	23	0.4	85	<1	2.95	198	1,044	22	225	76	205
R2	492	0.9	1,110	135	23	0.3	97	<1	3.16	51	257	36	206	89	152
R3	372	0.9	833	71	41	<0.3	100	<1	3.04	59	189	31	253	83	110
R4	533	0.6	483	215	13	1.1	84	<1	2.94	708	155	8	91.7	105	248
R5	365	0.7	504	480	11	0.6	197	<1	3.57	1,003	191	15	65.5	118	1,130
R6	340	6.5	71.5	405	8	2.8	826	<1	4.47	331	183	<3	4.2	216	1,804
R7	984	4.0	122	230	46	4.6	957	<1	2.73	939	8,744	5	18.9	83	1,870
R8	233	1.2	606	185	14	0.0	130	<1	2.79	731	1,092	16	122	106	356
R9	246	0.3	634	375	21	0.6	70	<1	3.40	519	168	22	221	136	206
R10	438	0.4	977	120	31	0.3	85	3	3.32	57	283	29	244	94	247
R11	444	0.7	555	105	13	<0.3	71	<1	2.39	100	180	16	89.3	67	91
R12	644	1.0	678	100	18	0.5	105	<1	2.76	206	553	17	115	72	185
R13	968	0.9	528	95	15	0.5	101	3	2.30	217	402	18	88.6	68	173
R14	340	1.6	859	165	53	0.6	133	<1	3.38	123	431	26	221	97	264
R15	175	0.9	829	250	20	0.7	87	<1	3.19	73	510	27	159	90	381
Mean	472.3	1.4	679.9	202.0	22.7	0.8	202.0	–	3.0	346.6	924.1	19.0	141.6	97.8	472.9
Min	175.0	0.3	71.5	71.0	8.0	<0.3	70.0	<1	2.3	51	155.0	<3	4.,2	66.0	91.0
Max	984.0	6.5	1410	480.0	53.0	4.6	957.0	3.0	4.4	1,003	8,744.0	36.0	253.0	216.0	1,870
Sediments															
RS16	142	0.5	204	380	6	0.7	59	<1	3.00	747	311	<3	31.4	124	182
RS17	171	0.5	220	400	5	0.6	66	2	2.89	655	293	10	33.2	118	197
RS18	74	0.5	132	345	3	1.0	54	2	2.73	763	263	<3	19.3	120	207
RS19	364	0.8	470	250	14	0.7	85	<1	2.83	376	328	18	74.9	92	176
RS20	20	<0.3	61.3	305	<2	0.8	64	<1	2.45	441	131	<3	8.6	110	76
RS21	309	0.8	320	365	6	0.6	73	<1	2.82	702	332	8	51.6	98	198
RS22	268	0.7	241	390	5	0.8	65	<1	2.45	405	217	6	36.0	98	195
RS23	346	0.9	464	330	13	0.7	95	<1	3.11	511	612	11	64.3	110	209
RS24	575	1.0	352	365	9	0.8	87	<1	2.82	635	439	12	55.2	119	174
RS25	509	1.0	794	165	19	0.4	108	<1	3.34	448	588	24	130	77	153
RS26	435	0.8	507	430	18	0.6	94	<1	3.44	550	579	16	89.1	114	232
RS27	765	1.3	540	405	21	0.9	96	<1	3.15	630	725	18	88.7	114	197
RS28	242	1.3	400	320	18	0.6	80	<1	3.14	645	380	12	65.4	103	237
RS29	38	0.7	132	620	5	1.3	77	<1	2.86	616	336	<3	14.5	126	259
RS30	435	1.1	581	145	18	0.4	70	<1	2.65	127	204	17	89.8	69	117
Mean	296.0	0.7	345.5	336.8	10.5	1.1	172.5	–	2.8	583.9	379.2	8.5	53.5	104.1	241.2
Min	20.0	<0.3	61.3	145.0	<2	0.4	54.0	<1	1.9	127	82.0	<3	4.1	69.0	76.0
Max	765.0	1.3	794.0	620.0	21.0	6.8	1,664	2.0	3.4	908	725.0	24.0	130.0	126.0	1,114
CEX	867	2.6	1330	<50	33	1.8	206	<1	3.4	381	3,190	<3	283	70	432
NCD	11.0	<0.3	24.1	825	<2	0.8	12	<1	1.08	208	19	<3	2.1	43	4
NIL (*)	–	15[a]	55	625	–	12	190	10	–	–	530	100[a]	15	250[a]	720

Values in mg/kg except Fe (%) and Au (µg/kg)

NIL(*) The Netherlands soil intervention values, *NCD* non-contaminated soils, sampled in old alluvial sediments far away the mining area, *CEX* tailings used in the column experiments

[a] Indicative level of serious contamination

Table 2:Concentrations of metals and metalloids in mineralization and mining wastes of Rodalquilar (Alemría, Spain)

	Au	Ag	As	Ba	Bi	Cd	Cu	Hg	Fe	Mn	Pb	Se	Sb	V	Zn
Mineralization															
Q-Cerro Cinto[a]	5,910	15	551	286	2	<0.3	52	<1	4.29	312	370	43	33.7	16	26
Q-Consulta[b]	5,270	34	33.7	198	<2	661.6	6,374	<1	2.41	233	48,770	<3	30.8	11	99,553
Q-M[a] Josefa[b]	1,190	40	658	429	<2	17.5	4,574	<1	4.53	371	2,629	19	570	10	2,847
Q-Las Niñas[b]	4,420	61	1,040	<50	157	62.6	2,190	<1	0.98	43	>5,000	<3	980	15	265
Mining wastes[c]															
Mean	1,466.6	2.9	325.7	236.2	13.6	0.53	208.8	0.8	4.47	336.6	1,339.1	21.3	31.2	83.2	120.2
Min	15.0	0.3	53	50	2	0.3	13	0.5	0.76	5.0	38	3	4.8	10	1
Max	3,840	5.6	1,700	1,000	37	1.5	485	3.0	14.3	2,226	>5,000	150	110	183	599

Values in mg/kg except Fe (%) and Au (µg/kg)

[a] Main high-sulfidation mineralization

[b] Low-sulfidation veins with galena, sphalerite, pyrite and calcopyrite

[c] Host-rocks and low-grade stockpiles

4.3 Groundwater

The analysis of groundwater samples taken from the alluvial aquifer revealed high concentrations of Al, As, Cd, Fe, Hg, Mn, Ni, Pb, Se, Sb and Zn (Table 3) and very high concentrations of chloride and sulfate (Table 4), above the European standards for drinking water (Real Decreto 149/2003, Boletín Oficial del Estado, BOE, 21/02/03). We also detected high values of Au, Cu, V and Zn in groundwater samples.

The results from field studies (Table 4) indicated that pH is neutral-alkaline and ranges between 6.7 and 8.3. The exception to this is the surface water sample, S-13, which had a low pH representing the conditions of acidic drainage at the old mine, Blanca y Negra. The field-measured redox potential indicates moderate oxidant conditions, except in S-6 and S-9 samples, obtained from deep wells and S-10 and S-14 samples, associated with possible organic dumps. Electrical conductivity varies considerably between samples W-15 (sea water) and S-13; the samples with the highest values were those taken close to tailings impoundments (S-18) or those affected by marine intrusion (S-7 to S-12). The temperature varied considerably, between 14 and 23 ºC in sample S-6, possibly due to the influence of the current geothermal system.

The major ion chemistry showed that groundwater samples had high concentrations of chloride, sulfate, Ca, Mg and K (Table 5). The samples with marine intrusion (S-7, S-11 and S-12) contained chloride concentrations above 1562 mg/L and Mg concentrations above 200 mg/L. The salinization of groundwater near the shoreline may have been caused by the elevated groundwater pumping in the area with a scarce recharge potential.

The distribution of the higher Cd, Fe, Mn, and possibly Cu concentrations in the groundwater from samples S-6, S-9, S-13, S-14 and S-18 (Table 4) is associated with the low Eh levels (except in samples S-13 and S-18). This possibly indicates that the dissolution of Fe and Mn oxyhydroxides may be the main cause of the elevated concentration of these metals in the groundwater. Furthermore, the very low concentrations of nitrate and high concentrations of dissolved Fe and Mn may be an indication of the reducing condition in part of the aquifer. There is no clear relationship between the distribution of total As and the possible reductive dissolution of Fe and Mn; the highest concentrations of As (>10 µg/L) are found in those groundwater samples with elevated concentrations of Fe and Mn (samples S-1, S-6, S-7 and S-13) and samples with low-to-medium concentration of Fe and Mn (samples S-11, W-16 and W-17). Thus, the arsenic concentration of Bangladesh groundwater is well correlated with Fe, Mn, and Al oxides in fine particle sediments

and TOC (total organic carbon) in large particle sediments (Anawar et al., 2003), contributing different phases to the total arsenic concentrations in groundwater.

High concentrations of Al (>0.4 mg/L) are associated with Ni-rich groundwater and surface water samples (S-6, S-13, S-14 and W-17). High concentrations of Fe were also found, which suggests a possible control of Ni by Fe and Al oxyhydroxides in groundwater. Moreover, sea water samples (W-15) contained high concentrations of Ni and Cu; this has also been reported in other Mediterranean areas (Carbonell and Navarro, 2001). High Pb and Zn concentrations are also associated with high Fe groundwater samples (S-1, S-6 and S-9), which indicate a possible sorption mechanism of Pb, and Zn control by Fe oxyhydroxides.

Table 3 Metal concentrations of groundwater.

Sample	Au (μg/L)	Al (μg/L)	Ag (μg/L)	Cd (μg/L)	Cu (μg/L)	Ni (μg/L)	As (μg/L)	Se (μg/L)	Sb (μg/L)	Pb (μg/L)	Fe (μg/L)	Mn (μg/L)	Hg (μg/L)	V (μg/L)	Zn (μg/L)	Cr (μg/L)
S-1	<0.02	<20	<2	1.6	13	5	12	7	3.1	14.7	1,900	730	<2	29	426	19
S-2	1	60	<2	<0.1	83	645	6.3	25	2.7	2.9	1,300	1750	<2	9	108	34
S-3	<0.02	<20	<2	<0.1	24	9	0.3	10	2.7	0.4	400	< 1	<2	5	190	15
S-4	0.08	<20	<2	<0.1	10	4	1.6	8	6.4	0.3	500	10	<2	4	99	13
S-5	0.08	30	<2	<0.1	10	< 3	2.8	4	6.3	0.8	1,000	3	<2	4	33	13
S-6	0.21	2,890	<2	5	65	119	16.5	< 2	2.4	22.3	76,300	416	<2	7	125	6
S-7	0.13	90	<2	0.2	18	39	13	< 2	2.4	1.6	10,200	115	<2	2	191	10
S-8	<0.02	< 20	<2	< 0.1	4	< 3	1.4	< 2	2.7	1.2	100	14	<2	4	62	12
S-9	<0.02	40	<2	2.4	22	42	2.1	< 2	2.7	21.7	46,100	624	<2	4	297	<5
S-10	<0.02	<20	<2	<0.1	14	4	< 0.3	< 2	3.1	8.4	5,500	70	<2	<1	83	<5
S-11	0.22	350	<2	<0.1	21	4	224	< 2	3.9	8.2	800	45	<2	8	79	11
S-12	0.11	130	<2	<0.1	17	< 3	< 0.3	< 2	2.6	1.7	300	107	<2	4	67	16
S-13	<0.02	>20,000	<2	62.1	1,300	95	66.1	18	0.9	3.9	4,800	912	<2	11	>2500	17
S-14	<0.02	400	<2	1.2	9	24	7.1	<2	0.2	2.9	73,500	519	<2	<1	146	<5
W-15[a]	<0.2	5,800	<20	<1	90	130	<3	<20	<1	35	4,000	540	<20	<10	70	<50
W-16[b]	0.07	260	<2	0.3	11	6	71.7	<2	2.9	8.5	200	10	<2	4	17	<5
W-17[b]	<0.02	490	<2	0.2	11	18	14.3	4	3.7	9.6	<100	142	4.0	4	58	26
S-18	<0.02	<20	<2	0.1	4	54	<0.3	<2	0.3	2.5	62,200	1720	<2	<1	12	<5
EDWS	–	200	–	5.0	2,000	20	10	10	5	10	200	50	1.0	–	–	50.0

Table 4 In situ determinations and main anions in groundwater.

Sample	Conductivity	pH	Eh	T (°C)	Na	Mg	K	Ca	Cl	NO_3	SO_4	HCO_3
S-1	<0.02	7.7	136	15.6	>300	78.6	23.3	90	711	<0.1	465	201
S-2	1	7.6	134	16.5	>300	>200	92.6	>200	3,983	<0.1	1,851	623
S-3	<0.02	7.6	136	–	>300	144	19.5	>200	848	<0.1	874	295
S-4	0.08	7.8	121	–	>300	185	21.3	>200	1,086	<0.1	717	189
S-5	0.08	7.8	110	–	>300	183	20.7	>200	217	<0.1	100	191
S-6	0.21	7.1	−40	23.0	>300	>200	19.4	>200	1734	<0.1	1,082	122
S-7	0.13	7.7	40	20.8	>300	>200	27.9	>200	1562	<0.1	640	202
S-8	<0.02	8.3	112	18.2	174	46.7	11.0	91	335	<0.1	164	190
S-9	<0.02	8	−20	22.7	>300	86.5	21.5	114	720	<0.1	507	334
S-10	<0.02	7.4	0	20.9	>300	>200	22.3	>200	1,612	<0.1	1,212	259
S-11	0.22	8.1	135	14.0	>300	>200	77.8	>200	1,645	<0.1	1,299	395
S-12	0.11	8.2	147	14.3	>300	136	26.5	131	1,981	<0.1	127	531
S-13	<0.02	3.1	280	–	20.8	20.6	1.8	51	24.6	11.9	1,350	<2
S-14	<0.02	6.7	−45	–	350	142	11.0	>200	1,770	1.3	1,030	<2
W-15[a]	<0.2	8.1	74	19.8	10,500	1,510	461.0	860	20,400	8.8	2,830	122
W-16[b]	0.07	–	–	–	350	36.8	25.5	80	974	0.8	161	56
W-17[b]	<0.02	–	–	–	216	24.2	21.2	155	1,870	28.3	704	226
S-18	<0.02	6.97	210	–	>350	187	19.5	110	1,190	<1.3	1,120	65
EDWL	–	–	–	–	200	–	–	–	250	50	250	–

Values in mg/L, Eh in mV

EC electrical conductivity in mS/cm, *EDWS* European drinking water standards

[a] Sea water

[b] Superficial water of lagoons near the Playazo beach

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